Baseline

Baseline arsenic levels in marine and terrestrial resources from a pristine environment: Isabel Island, Solomon Islands

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ABSTRACT

Baseline records are crucial in understanding how chemicals of concern impact on the receiving environment. We analysed terrestrial and marine resources from a pristine site on Isabel Island, Solomon Islands, to provide environmental baseline levels for total arsenic and arsenic species composition for commonly consumed marine resources. Our data show that levels of the more toxic inorganic arsenic species were very low or below detectable limits, with the exception of the seaweed *Sargassum* sp. that contained pentavalent inorganic arsenic levels of 4.63 $\mu g\,g^{-1}$. Total arsenic concentrations in the majority of marine and terrestrial samples collected were below 2 $\mu g\,g^{-1}$. The less toxic arsenobetaine was the predominant arsenic species present in all marine fauna samples analysed. This work highlights the need for arsenic speciation analysis to accurately assess potential toxicity of marine resources and provides a crucial baseline to assess the impact of future development within this region.

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Few of the world's marine environments are unaffected by some level of industrial or agricultural activity, therefore true baseline measurements in the absence of anthropogenic influences are difficult to obtain. When contaminants are naturally occurring, as well as anthropogenic (as is the case with arsenic), distinguishing between natural and human sources of contamination can be challenging. In recent years, several studies have documented the environmental and human health impacts of both natural and anthropogenic arsenic contamination. For example, Anawar et al. (2002) estimated that 9 million people living in Bangladesh were exposed to groundwater containing arsenic at levels that are known to have long-term health risks and is recognised as one of the largest cases of mass poisoning in history (Smith et al., 2000). In Canada, arsenic levels have been recorded between one to three orders of magnitude above acceptable limits due to the release of arsenic from mine tailings associated with past gold mining (Wang and Mulligan, 2006). Arsenic contamination was also responsible for the potential exposure of 10 million people to chronic arsenic poisoning from the Red River and Mekong River in Vietnam and Cambodia (Berg et al., 2007). These and other instances have highlighted the importance of monitoring for arsenic within the environment and food products worldwide.

A ubiquitous element, arsenic is the 20th most abundant element on earth, where it predominately occurs in its inorganic

forms within the earth's crust (Mandal and Suzuki, 2002). However, arsenic is released into the environment by weathering, geothermal activity, microbiological activity, mineral extraction processes, and the combustion of fossil fuels (Matschullat, 2000; Mandal and Suzuki, 2002; Bhattacharya et al., 2007). Arsenic is well known historically due to its potentially harmful and toxic effects on living organisms, with written records of the toxic properties of arsenic dating back to 222 BC (Matschullat, 2000). In 1993, World Health Organisation guidelines noted that ingesting food or water containing more than 0.01 mg L^{-1} of inorganic arsenic was harmful to the body, while an inorganic arsenic content exceeding 60 mg L^{-1} could be fatal (FAO/WHO, 2000). However, arsenic is also intrinsic in the production of everyday products; such as metals, pesticides, glass, and electronic components, therefore its use and extraction remains unavoidable (Matschullat, 2000; Bhattacharya et al., 2007). Direct anthropogenic extraction of arsenic has been estimated at over 30,000 t year^{-1} globally (Matschullat, 2000), although the total turnover of arsenic is likely to be much higher. Arsenic concentrations in marine waters are relatively stable and are typically below 2 $\mu g\,L^{-1}$ (Ng, 2005). Higher arsenic concentrations are typically found in some estuarine waters due to freshwater and terrestrial sediment inputs, which can contain higher arsenic concentrations, particularly when in close association with industrial or mining activities (Smedley and Kinniburgh, 2002).

Arsenic occurs in a number of organic and inorganic forms and these vary in their toxicity towards humans. The majority of studies

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have focussed on the inorganic arsenite (As^{III}) and arsenate (As^V) salts, as well as the organic forms monomethylarsonic acid (MMA), dimethylarsonic acid (DMA), arsenobetaine (AsB), and arsenosugars (AsS). In general the order of toxicity for arsenic forms are $As^{III} < As^V < DMA < MMA < AsB < AsS$, with As^{III} approximately 50–180 times more toxic than DMA and MMA, and approximately 700-fold more toxic than AsB (Benramdane et al., 1999). However, this is not without contention and is dependent on the oxidation state of the organic arsenic species involved (Mandal and Suzuki, 2002). Unsurprisingly due to its toxicity and potential to cause harm to humans, determining arsenic levels within the environment, food, and arsenic exposure thresholds have been the focus of much research. Acute arsenic toxicity is well documented (Smith et al., 1992), however, illnesses as a result of chronic exposure to arsenic is more difficult to establish. Furthermore, following exposure arsenic is metabolized and converted into other forms of arsenic making the causative arsenic form difficult to ascertain (Mandal and Suzuki, 2002). Nonetheless, acute exposure to arsenic is known to be linked to a number of human diseases including skin lesions, black foot disease, and cancers of the brain, liver, kidneys, and stomach (Smith et al., 1992; Ratnaike, 2003). Consequently, safe standards for the concentration of arsenic in drinking water and foods are established within a number of countries. For example, the World Health Organization's recommended upper limit for total arsenic in drinking water of $10\ \mu g\ L^{-1}$ (WHO, 2012) and the maximum recommended levels for total arsenic in foods (excluding seafood) within the UK are $1\ \mu g\ g^{-1}$ (MAFF, 1959). However, standards rarely take into account the relative toxicity of the arsenic species present and standards are usually set on total arsenic concentration. Yet, marine food stuffs generally contain low or undetectable levels of As^{III} and As^V, and contain higher concentrations of the less toxic AsB. Therefore, recent studies have questioned the appropriateness of setting seafood safety standards based on total arsenic concentration (Peshut et al., 2008). Exceptions are the standards for Australia and New Zealand where arsenic safety standards are set specifically for inorganic arsenic. These standards also vary by seafood category with upper limits for inorganic arsenic of $1\ \mu g\ g^{-1}$ for seaweeds and molluscs, and $2\ \mu g\ g^{-1}$ for crustaceans and fish (FSANZ, 2013).

The Solomon Islands, in the South-west Pacific, comprises of an island group accounting for a total land area of 28,400 square kilometres. Selective commercial logging is the predominant industry within the Solomon Islands, however, logging resources are becoming rapidly depleted (DFAT, 2004). Few commercial industries other than logging have been developed in the economy of the Solomon Islands. Gross domestic product is less than $2 billion US dollars per year and it is ranked 194th in the world (Central Intelligence Agency, USA, 2013). Over 75% of Solomon Islanders lead a subsistence lifestyle and are heavily dependent on terrestrial gardens and marine resources for food, evidenced by one of the highest fish consumption rates in the world, with 82.4% of meals containing animal protein of fish origin (Richards et al., 1994). Due to the rapid decline of timber resources and population expansion in the Solomon Islands, alternative economic revenues from fisheries and mineral resources have been proposed as possible areas for economic development (DFAT, 2004) prompting the need for baseline environmental assessment in this area.

In this study we report levels of total arsenic ($As_{[Total]}$) and arsenic species composition in a wide range of commonly consumed fish and shellfish from Isabel Island, Solomon Islands. In addition, we test arsenic levels in sediment, marine waters, marine plants/algae, as well as commonly consumed terrestrial plants to gain a broad environmental baseline for the region. This study therefore provides arsenic baseline data for Isabel Island and an important tool for monitoring environmental change of the Solomon Islands marine resources.

The study area stretched a 36 km length of coastline on the western side of Isabel Island and extended 7 km seaward. The study site was adjacent to several rural villages (the two largest consisting of Jejevo and Hurepelo, respectively) and included important fishing grounds for these villages (Fig. 1). The study location contained fringing reefs, outer barrier reefs and an inner lagoonal back reef. The area was typically dominated by coral habitat; however mangrove and seagrass habitats were also present within the site. The adjacent terrestrial catchments were typically steep with native forest with small cleared areas for villages.

A range of environmental, flora and faunal samples were collected from both terrestrial and marine habitats within the study site. Sampling for seafood was conducted during three trips to Isabel Island in March, May and August 2013. Sediment and marine surface water samples were collected in May and August, and August and November 2013, respectively. Terrestrial sampling composed of fruits and vegetables commonly consumed by villagers collected during March and May 2013.

Marine surface waters were collected from 10 sites within the study area using sterile syringes. Marine sediment samples (50 g) were obtained from the top 5 cm of the sediment from six offshore and 12 inshore sample sites. Water and sediment samples were stored at $-20\ °C$ in sterile HDPE containers prior to analysis. Marine fish and shellfish samples from a wide range of target species from multiple trophic levels were also collected (Fig. 1). Seafood samples included only mature specimens typical of the size range and age of those caught by local fishers. Seagrass and macroalgal samples were also collected from the sample site. Following collection all terrestrial and marine resource samples were stored at $-20\ °C$ prior to analysis. A summary of sample locations and timing are presented in Table 1.

Fish and shellfish samples were rapidly dissected to remove shell, skin or gut from the sample to provide a 50 g section of muscle tissue, with the exception of *Polymesoda erosa* (Mangrove cockle) for which both muscle and gut tissue was included within the analysis to better represent what is typically consumed. Marine plant/macroalgal samples (*Enhalus acoroides*, *Zostera muelleri*, *Halophila* sp., *Thalassia hemprichii*, *Caulerpa* spp. and *Sargassum* sp.) were obtained by the collection of 50 g sections of leaf or thalli from shallow lagoon areas. These samples were rinsed thoroughly with seawater prior to collection to remove any attached sediment that might affect arsenic analysis. Whole fruit of terrestrial plants (including the Orange Mangrove, *Bruguiera* sp.) were also collected for subsequent analysis.

Arsenic analysis was conducted by Queensland Health, Forensic and Scientific Services (Queensland, Australia) within a NATA-accredited laboratory. All measurements were conducted following appropriate QA/QC standards. All collected samples were assessed for $As_{[Total]}$ using ICP-MS. Samples containing detectable levels of $As_{[Total]}$ were then further analysed by HPLC-ICP-MS to determine arsenic speciation. Detection limits for $As_{[Total]}$ were $0.05\ \mu g\ g^{-1}$. Detection limits for As^{III}, As^V, DMA, MMA and AsB varied depending on sample dilution but ranged between 0.05 and $0.2\ \mu g\ g^{-1}$. All results are presented as means with standard deviation unless otherwise stated.

In this study, all samples from edible terrestrial resources contained $As_{[Total]}$ values below the detectible limit of $0.05\ \mu g\ g^{-1}$ (Table 2) and were not further analysed for arsenic species content. Mean $As_{[Total]}$ measurements of marine surface water within the study site were 1.67 ± 0.37 and $1.65 \pm 0.32\ \mu g\ L^{-1}$ over the 10 sample locations for August and November, respectively. In addition, inshore marine sediment samples contained higher mean $As_{[Total]}$ level of $18.31 \pm 13.93\ \mu g\ g^{-1}$ compared to offshore sediments ($3.18 \pm 1.24\ \mu g\ g^{-1}$).

The lowest level of $As_{[Total]}$ within macroalgae and seagrass was found in *Z. muelleri* at $0.27\ \mu g\ g^{-1}$. Conversely the highest levels